

Idaho Department of Quality
P4 Production Southeast Idaho Mine sites
Data Validation Comparison

Diane Short & Associates (DSA) has reviewed a client-specified selection of 18 data sets which represent approximately 10% of the data sets from the P4 Production Southeast Idaho Mine sites. Full review of all data sets for the project were reviewed by Montgomery Watson (MWH), Bellevue Washington. The review includes comparison of the DSA validation findings with those contained in the report 'Phase I Site Investigation Summary Report, April 2005 (9/20/06 Revision)', "October 2005 Groundwater data Validation Summary, Final" and "May 2006 Data Validation Report".

As noted to the Idaho Department of Environmental Quality (IDEQ), the data provided to MWH and to DSA from the analytical laboratory, ACZ of Steamboat Springs, Colorado, were in a non-standard format. QC items were not grouped according to type (eg. Matrix spikes, Method blanks, etc.) but instead were reported by analyte. In addition, the preparation batches (called work groups, WG), were not linked to the reported data and the correct quality control (QC) could only be determined by date. If more than one WG was prepared or analyzed on the same date, the QC could not be distinguished without a full raw data review. This format also did not allow for a productive or clear assessment of missing QC items as some QC items were present for some analytes and not for others in the same data set. The review, therefore, required extensive time to perform and to find missing QC and to apply qualifiers to the correct WGs (QC batches).

The DSA report is being used as a template to relate missing or incomplete review per the MWH reports. If an item is completely missing from the MWH reports it is highlighted. If an item is incomplete, a comment will be included in [brackets]. There were 2 SDGs that DSA was not able to find as noted in the MWH reports. This includes 58640, water, and 47720, vegetation. It is assumed that similar comments apply to these SDGs even if they are not highlighted. It is noted that for the May 2006 report, more of the required QC items are noted and MWH started to include values for at least the blanks although there is no evidence of addition of qualifiers to the data in the provided tables. The reports also do not supply an indication of associated biases or data usability impacts of the noted QC items.

Data Impacts in summary for the missing or incomplete items noted in the report:

Blanks – missing blanks result in false positive data being reported. This is a conservative impact and results in data being reported for potential clean up that are not real values.

Interference Check Sample Serial Dilution – these apply only to samples with very high values for mostly the big cations (aluminum, calcium, barium, sodium, iron). For most of these samples, only a limited list of analytes is reported. If an ICS was out of limits, the impact could not be determined without reprocessing the data to look for the potential interfering analytes. It is required, however, to run the ICS to ensure that the instrument software is adequately compensating for wavelength overlaps.

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Serial Dilution – these apply only to reported values that are at least 50 to 100 x the Method Detection Limit (MDL). Most of the reported values that are in that range are analytes like calcium and magnesium. If these are not analytes that could be used for project decisions, the impact is not significant even though this is a required validation item. For the serial dilutions that were reported by DSA, they had a positive impact on the data, which means potentially high biases are reported in the data. These would be conservative values as they could be higher than the actual values.

Lack of values to QC outliers – the potential high or low bias to the data cannot be determined. For high spikes, this is a conservative impact and high values could be reported. If low spikes are found, however, a low bias could mean that the reported value does not fully represent the amount of the analyte in the sample.

CRDL Standard – without a verification of the low level standard, the data reported > MDL and < RL could have a higher degree of variability and only values > RL can be used as accurate values. From this limited review, there are some analytes whose low level values cannot be verified. This could apply to other data sets. As no QC limits were in place for the 1994 validation guidance (which appears to still be in place for the 2004 validation), the reviewer may not be accountable for the review of this item.

ICPMS tune and Internal Standard data – the full verification of the instrument calibration and tuning cannot be assessed and the potential matrix effects that can be inherent in mass spectral analysis cannot be determined. These items were acceptable for the data sets reviewed by DSA and these criteria are expected to be acceptable.

INORGANIC DATA QUALITY REVIEW REPORT

SAMPLE DIGESTION NUMBERS: 45773, 45774, 45832, 46912, 45918, 46807, 46940, 47351, 47669, 47715, 47720, 47726, 47824, 54005, 56408, 56513, 58640, and 58644

PROJECT: Idaho Dept. of Quality, P4 Production, SE Idaho Mine sites

LABORATORY: ACZ Laboratories, Steamboat Springs, CO

SAMPLE MATRIX: Water (total and dissolved), soil, plant, animal tissue

SAMPLING DATE (Mo/Yr): 9/04, 5/06 NO. SAMPLES: 118 (w), 32 (s), 18 (Animal, fish Tissue), 33 (Plants), 2 (Veg)

ANALYSES REQUESTED: USEPA SW846 Method ICP 6010B, ICPMS 6020, CVAA 7470A Mercury; Standard Method HGAA 3114 for selenium; MCAWW Method 300.0 IC for IDEQMET0208

sulfate

SAMPLE NUMBERS: See Attachment

DATA REVIEWER: Joseph J Egry IV, Diane Short

QA REVIEWER: Diane Short & Associates, Inc. INITIALS/DATE: _____

Telephone Logs included Yes _____ No X

Contractual Violations Yes _____ No X

The EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, 2002 (SOP) and the requested SW-846 Methods (1994 and current updates) and MCAWW methods, plus the project QAPP have been referenced by the reviewer to perform this data validation review. The review includes evaluation of calibration, holding times and QC for all samples and review, where applicable, of interferences for 10% of the samples and a 10% review of transcription and calculation algorithms. Determining the exact analytical sequence (sequencing) was done, where applicable, on 10% of the data. General comments regarding the data/ analytical quality are part of the review when raw data are submitted. The EPA qualifiers have been expanded to include a descriptor code and value to define QC violations and their values, per the approval of the project Manager.

NOTE: Those items in this report, which have an asterisk (*), are specific to ICP/MS.

I. DELIVERABLES

A. All deliverables were present as specified in the Statement of Work (SOW) or in the project contract.

Yes X No _____

The following is noted for general clarification:

Water samples were analyzed for up to 12 ICP metals and 11 ICP/MS metals, plus mercury, selenium and sulfate parameters. Most water sets also contained total and dissolved analyses with associated distinct QC sets (days of analysis with separate QC and calibration). There were also a number of data sets that contained multiple runs (QC sets) for one of more of the requested analytes. The associated QC batch of these multiple QC sets was used in qualification of data. The following is a breakdown of matrices submitted.

Method	Water	Water	Soil	Plant	Animal	Veg
ICP &/or ICPMS Metals	Total 80	Diss. 49	32	9	4	2
Se by AA	108	59	42	33	18	2
SO4	33					

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The standard deliverable for analytical data is to provide summary tables for each of the following QC items: calibrations, low level standard check, blanks, Matrix spikes and matrix duplicates (or MS dups), post digestion spikes, LCS, serial dilution, ICP ICS and ICPMS Internal Standards as well as tables for the current MDLs and RLs. The laboratory has instead generated data lists for each analyte including the above items when they were actually analyzed. As many of the above items are missing from the data sets, and are not consistently missing for all the analytes in the data set, the complexity of the review was significant and time consuming. A listing of missing QC is contained in the specific QC sections of the report.

II. ANALYTICAL REPORT FORMS

A. The Analytical Report or Data Sheets are present and complete for all requested analyses.
Yes X No

B. Holding Times

1. The contract holding times were met for all analyses (Time of sample receipt to time of analysis)

Yes No X

See below. Samples were received within 1 – 3 days of collection, but not analyzed within contractual holding time for L47824.

2. The applicable method holding times were met for all analyses (From time of sample collection to analysis).

Yes No X

The following holding times had been exceeded.

SDG	QC Set	Sample	Analyte	Date Sampled	Date Analyzed	Qualifier
L47824	180026	SWMST275-0-F	Sulfate	9/14/04	10/19/04	JH5
L54005	199814	103005GWMMW004-2-F	Sulfate	10/30/05	11/28/05	JH1
		103005GWMMW004-3-F	Sulfate	10/30/05	11/28/05	JH1

[last item noted, but no value given to days over hold time]

Data is qualified JH#, where # is the number of days exceeding the holding time. Data could possibly be biased low as the number of days exceeds the allowed holding time.

3. Samples were properly preserved to pH < 2, or applicable preservative was used and were at the required temperature.

Yes No X

For L47720, the temperature was 15.8° C. These samples are noted as 'veg', but treated for preparation and reporting as aqueous. They are also reported at pH < 2 as if they are water. If these are not water-type matrices, they should be kept at < 4 ° C. There is a note that the project

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manager is to be contacted, but there is no follow up communication. As these appear to be of some type of water matrix, no qualification is added. One of the samples is an equipment blank, which would be a water.

C. Chains of Custody (COC) [No chain of custody or sample integrity comments are present in the MWH reports]

1. Chains of Custody (COC) were reviewed and all fields were complete, signatures were present and cross outs were clean and initialed.

Yes ☐ No ☒

Chains contain items that have been blocked out rather than one-line cross out and no initials are present. The chains have a gap from date of relinquishment to date of laboratory receipt. Some of the chains note a FedEx courier and some do not, none have a FedEx airbill number for tracking of the sample custody. The chains need to be updated and completed for the project record.

For the majority of the data sets there is no method of analysis listed on the chain. As almost all chains are impacted, they have not been listed here. In the box which usually has the requested method of analysis, it only lists items like "soil, SW total, SW dissolved, fish, etc". The reviewer cannot verify that that required or requested analyses have been performed.

L56513: There are 2 samples on the chain that are noted as not being received and it is noted that the client was not notified.

L47720: There are 10 samples listed on the chain, but only 2 are reported. There is no method of analysis listed on the chain. In the box which usually has the requested method of analysis, it only lists "Veg". [This SDG not found in reports]

III. CALIBRATION AND STANDARDIZATION - ICP/MS

A. Initial Calibration -ICPMS

*1. Mass calibration and resolution checks for both low and high mass isotopes and are within 0.1 amu of the true value

Yes ☒ No ☐ NA ☐

[This item is only included in the May 2006 report and is checked as being reported, but it is also checked that no tune was performed. The comments are in contradiction. DSA has found this in the full raw data review of 56513, which is part of the report]

*And produced a peak width of approximately 0.90 amu at 10% peak height.

Yes ☒ No ☐ NA ☐

Per the full raw data review of 2 of the data packages:

L47726: Only the tune from 11/24/04 is reported. There are no tunes for 11/18, 11/29 or 12/05 reported analyses. Full evaluation of calibration and instrument tuning cannot be determined.

L56513: Full tunes are reported for 12/ 19 and 22/06.

*2. Instrument stability: tuning solution was run a minimum of four times and RSD of absolute signals for all analytes was less than 5%.

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Yes ☒ No ☐ NA ☐

% RSD are reported for

L5651: 9Be, 24Mg, 59Co, 115In, 208Pb

L47726: 5Li, 59Co, 115In and 205Tl

[The % RSD is only included in the May 2006 report and is checked as being reported. That no tune was performed is also reported, which would contradict this finding. DSA has found this in the full raw data review of 56513, which is part of the report]

B. Internal Standardization

*1. A minimum of three internal standards were present in all standards and blanks at identical levels.

Yes ☒ No ☐ NA ☐

The Internal Standards are different from data set to data set. When there is a short list of metals requested, only the IS's associated with the requested analytes are reviewed.

*2. The intensity of each internal standard was within the 60 - 120% method limits in the CCV compared to the IC blank or standards.

Yes ☒ No ☐ NA ☐

C. Instrument tune.

*The tune check was run.

Yes ☒ No ☐ NA ☐

[This is noted as not having been performed, it was performed for the sets DSA reviewed]

*And the Rhodium counts were $\geq 50,000$ counts in the standards and the % RSD of 24Mg, 103Rh and 208Pb signals are less than 5%.

Yes ☒ No ☐ NA ☐

The laboratory may also use 7Li, 58Co, 115In, and 205Tl. This is a raw data review item for only 10% of the data.

D. Initial Calibration – ICP and ICPMS

1. All initial instrument calibrations were performed as defined in the contract or Statement of Work (SOW). All re-analyses were performed if required.

Yes ☒ No ☐

2. Initial Calibrations (ICV) were within the 90 – 110% limits (80 – 120% for Hg, Se) and the CVAA, GHAA and wet chemistry, 3 to 5 point curves, the correlation coefficient must be >0.995 for the analysis to proceed.

Yes ☐ No ☒

The following analytes exceed the QC limits:

[MWH has used 89 – 111 instead of 90 – 110. This may be a rounding issue, but DSA has used the results as reported by the laboratory]

SDG	QC Set	Analyte	Recovery (%)	Qualifier
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L47824	179843	Cadmium	110.3	JC110
L45918	175879	Zinc	110.5	JC110
L47715	181460	Chromium	110.4	JC110

Data is qualified JC#, where # is the percent recovery of the Initial Calibration Verification (ICV) standard from the true value. The limit is 90% - 110%. Data whose percent recovery is less than 90% could possibly be biased low with respect to the extent of the recovery. Data whose percent recovery is greater than 110% could possibly be biased high with respect to the extent of the recovery. Undetected data are not qualified for high ICV recoveries. These are minimal exceedences and are not expected to impact the calibration or final data.

3. Continuing calibrations (CCV) were within 90 – 110 % (80 – 120% for Hg, Se)

Yes X No

4. The low level CRDL standard was analyzed and the 70 – 130% limits were met. [In the 1994 guidance, the CRDL standard is not qualified, but it is part of the review and is reported if it is missing. The 2002 guidance does expand the review to include qualification limits. The 2002 NFG were in use during the time of the MWH review]

Yes No X

CRDLs are not consistently reported. This is called a PQV by the laboratory. There can be a PQV for one analyte in a data set, but not for others.

L56513: CRI not reported for most of the ICPMS analytes including: Cd, Cr, Pb, Mn, Ni; for ICP there is no CRI for dissolved Mn; no CRI for selenium or mercury.

L46912, L47351, L46807, L46940, L58644, and L58640: no CRI for Se.

L47726: no CRI for any analytes.

L47669: no CRI for any analytes.

L47824: no CRI for Cd, Cr, Ni, Se, V and Zn.

L45774: no CRI for Cd, Cr, Mg, Ni, Se, V, and Zn.

L54005: no CRI for Cd, Cr, Mn, Ni, Se, V, and Zn.

L45832: no CRI for Cd, Cr, Ni, Se, V, and Zn.

L45918: no CRI for Cd, Ni, Se, V, and Zn.

L47715: no CRI for Cd, Cr, Cu, Mo, Ni, Se, V, and Zn.

L45773: no CRI for Cd, Cr, Ni, Se, V, and Zn.

L47720: Per the full raw data review, no CRI (PQV) reported, but there is a PQV in the raw data.

The PQV has no final results reported, but the CPS values have been compared to the lowest reported standard (Std 3) and potential values extrapolated. The ability of the instrumentation to reach the low level standard is not acceptable for cadmium and molybdenum. The raw data were reviewed for the 2 client samples. Instrument counts, even in the range of the PQV, were not reported and the undetected values appear to be verified although the MDL may not be valid. Undetected values only to the reporting limit should be assumed for these samples.

The low CRDL standard is required to ensure accuracy of low-level response. Results reported

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>MDL but below the RL could be estimated values and false undetected values could be reported.

III. INTERFERENCES

A. Isobaric elemental and molecular interferences.

1. The data were free of isobaric elemental and elemental interferences as measured by the Interference Check Sample (ICS) for both ICP and ICPMS.

Yes ☐ No ☒

The ICS QC requirement has not been met for some of the data sets as noted below. When the ICS is not reported, it cannot be verified that the interference from high-level analytes has been adequately compensated for in the computer software. Only samples that have high levels of the major cations (Al, Fe, Ca, Na, K) would be most impacted. For the analyses with limited list of analytes, the potential interfering analytes are not in the project list and even if the ICS were out of limits, the potential impact could not be evaluated unless the raw data were re-evaluated for the interfering analytes.

[MWH reported acceptable ICS for many of the data sets, those noted below did not contain reported ICS results]

L56513: full list of analytes requested, no ICS reported.

L47824: no ICS reported.

L45774: no ICS reported.

L54005: no ICS reported

L45773: no ICS reported.

L47720: no ICS reported

And the ICS percent recoveries were within the required control limits of 80 – 120%.

Yes ☒ No ☐

2. Oxide check

*The concentration of Cerium Oxide is less than 10% of the Cerium concentration and the concentration of Ba+2 is less than 3% of Ba.

Yes ☐ No ☒ NA ☐

There is no evidence in the raw data that the oxides are analyzed or are used as required to minimize interferences.

B. Memory interferences

*1. Suitable rinse times were determined prior to sample analysis.

Yes ☒ No ☐ NA ☐

*2. Memory interferences and Chloride molecular interferences (ArCl and MoO) were assessed within the standard report.

Yes ☐ No ☒

There is no evidence in the raw data that these interfering molecules are analyzed for or are used as required to minimize interferences. All calibrations, LCS were will within limits which could indicate that the computerized correction for chloride has been performed.

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IV. BLANKS

Note: the highest blank associated with any particular analyte is used for the qualification process and is the value entered after the "B" blank descriptor.

A. The initial calibration blanks (ICB) and continuing calibration blanks (CCB) were analyzed at the required frequency.

Yes X No NA

The laboratory reports ICB, CCB or laboratory reagent blanks (LRB).

And the ICB and CCB results were within the required control limits (non detect to the MDL).

Yes No X NA

Below is a table of analytes that were found in the calibration blanks. See the EDD for final qualification.

SDG	QC batch	Analyte	Result	Qualifier
L56513	206448	Arsenic (dis)	0.00073	UCB.00073
		Lead (dis)	0.00014	None
	206701	Thallium	0.00015	None, ND
		[Analytes reported, but values are not those found in DSA review, Arsenic not reported]		
L54005	199080	Cadmium	0.00012	None, ND
L56408	205973	Arsenic (tot)	0.00067	None, ND

Data have been qualified UCB#, where # is the value of the associated blank. Data are qualified only when sample results are $<5 \times$ blank. When data are $>5 \times$ the blank and require no qualification, it is indicated as such in the table. Data are fully usable as undetected values.

B. Method Blanks were analyzed at the required frequency and for each matrix and analysis

Yes X No

And no Blank contamination was found in the Method Blank

Yes No X

Below is a table of analytes that were found in the preparation blanks. Note that preparation blanks are not required for dissolved metals. The following data sets did not have an identified preparation blank. Contamination cannot be verified and false detected values could be reported.

L56513, L54005, L45773, L47720 – An LRB is reported. Full review of the raw data preparation tables for one data set has confirmed this is a preparation blank that is carried through the entire preparation process.

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SDG	QC Set	Analyte	Result	Qualifier
L47726	180947	Chromium	2.77	None
Water	180947	Molybdenum	0.094	UB.094
	180947	Vanadium	3.91	None
	181486	Chromium	3.47	None
	182088	Chromium	0.083	None
	181486	Copper	1.98	None
	182021	Copper	2.57	None
	182382	Copper	2.19	UB2.19
		[Analytes noted for some, but no values]		
L47824	179842	Cadmium	0.00011	None, ND
GW		Chromium	0.00021	None, ND
		Nickel	0.00024	None, 5X
L54005	198985	Chromium (dis)	0.00021	UB.00021
Water	199080	Iron (tot)	0.047	None, 5x
		Aluminum (tot)	0.05	None, 5x
L45832	173710	Chromium	0.072	None, 5X
Soil		Nickel	0.89	None, 5X
		Vanadium	0.219	None, 5X
	173957	Chromium	0.051	None, 5X
		Vanadium	0.323	None, 5X
		[analytes noted, no values]		
L45918	173797	Vanadium	0.076	UB.076
fish	175879	Vanadium	0.248	UB.248
L47715	181460	Chromium	0.727	None, 5X
Soil	180983	Molybdenum	0.275	None, 5X
	181126	Molybdenum	0.052	None, 5X
	181460	Vanadium	1.242	None, 5X
		[analytes noted, no values]		
L56408	205973	Aluminum (tot)	0.033	None 5x
L56513	206212	Aluminum (tot)	0.031	UB.031
Water		Iron (tot)	0.021	UB.021
	206579	Chromium (tot)	0.00012	UB.00012

Analytes reported as contaminants in the preparation blank are qualified UB# in the affected samples, where # is the value of the blank corrected to the units of the sample. Sample detects

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whose values are less than 5x blank are qualified and are fully usable as undetected values at that level. 'None' indicates that undetected values or values > 5 x blank were reported. Data are fully usable as undetected values.

C. If Field Blanks were identified, no blank contamination was found

Yes ____ No X

Below is a table of analytes that were found in the field blanks. If there was not reported contamination, the blank is not listed.

SDG	Blank	Analyte	Result	Qualifier
L56513	050906SWMST088-EQ-F	Chromium	0.0002	None
		Manganese	0.0015	None
		Zinc	0.005	None
L45774	051204SWMSP011-EQ-F	Sodium	0.6	UFB.6
		Zinc	0.002	UFB.002
L45773	051204SEMSP021-EQ-U	Calcium	0.4	None
	051204SEMSP021-EQ-U	Chromium	0.0002	UFB.0002
	051204SEMSP011-EQ-U	Sodium	0.5	UFB.5
	051204SEMSP021-EQ-U	Vanadium	0.000009	None

Data have been qualified UFB#, where # is the value of the associated blank. Data are qualified only when sample results are <5 X blank. When data are >5 X the blank and require no qualification, it is indicated as such in the table. Data are fully usable as undetected values.

V. INTERNAL STANDARD RESPONSES

*1. The absolute response of the internal standard in the sample did not deviate more than 60-125% from the original response in the calibration blank or standard.

Yes X No ____ NA ____

*Or dilutions were performed as required by the method to minimize errors if the internal standard is naturally present in samples.

Yes ____ No ____ NA X

VI. MATRIX SPIKE

1. Matrix spike (MS) was analyzed for every analysis performed and for every 20 samples or for every matrix whichever is more frequent.

Yes X No ____

Note that an analytical spike is reported and is appropriate for the dissolved water samples.

B. The MS percent recoveries were within the limits defined in the contract or the CLP 75-125%.

Yes ____ No X

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The following matrix spike recoveries resulted in sample qualification. [MWH reports have no values so no bias can be determined. For some reports, the reviewer has noted when a recovery is out, but not qualified for the 4x criteria, and sometimes it is not noted.]

SDG	Matri x	QC set	Parent Sample	Analyte	Result	Qualifier
L58644	Water	213089	050406SWMSP059-0-U	Selenium	[74/85	JS74]
			050406SWMSP010-0-U	Selenium	85/240	None, 4X
L47669	Plant	180285	VEMST069-0-C(5)	Zinc	[54/56	JS54
L46940	Water	177338	Non-Client Sample	Selenium	70/67	JS67]
L46807	Plant	176602	VEMWD082-1-C(6)	Selenium	86/61	None, 4X
			Non-Client Sample	Selenium	55/100	None, 4X
L45832	Soil	173710	Non-Client Sample	Cadmium	[44/50	JS44]
			Non-Client Sample	Chromium	0/0	None, 4X
			Non-Client Sample	Nickel	52/91	None, 4X
			Non-Client Sample	Vanadium	0/0	None, 4X
			Non-Client Sample	Zinc	0/0	None, 4X
		173957	Non-Client Sample	Chromium	0/0	None, 4X
			Non-Client Sample	Nickel	61/100	None, 4X
			Non-Client Sample	Vanadium	0/0	None, 4X
L45918	Fish	173689	FIMST126-1-QA1(F)	Nickel	1200/35	JS1200
			050804FIMST126-1-QA2	Zinc	35/0	None, 4X
			050804FIMST126-1-QA3	Zinc	39/314	None, 4X
			050804FIMST126-2-0	Zinc	61/0	None, 4X
L47715	Soil	181460	SSMSG005-1-C(5)QA1	Chromium	133/149	None, 4X
			SSMSG005-1-C(5)QA1	Vanadium	131/141	None, 4X
		180983	SSMSG005-1-C(5)QA1	Zinc	238/191	None, 4X
L47726	Soil					Run 2x, ok 2 nd , no Q
		182382	SSMST236-0-C (9)	Copper	71/109	
		182088	SSMST236-0-C (9)	Chromium	137/ 193	None, 4x
		180947	SSMST022-1-C (6)	Chromium	127/ 138	None, 4x
		181486	SSMST022-1-C (6)	Vanadium	135/ 127	None, 4x
L56408	Water	205973	Non-Client Sample	Arsenic	141/122	None, ND
			Non-Client Sample	Nickel	0/0	None, 4X
			Non-Client Sample	Uranium	234/0	None, 4X
			Non-Client Sample	Vanadium	97/0	None, 4X
			Non-Client Sample [Nothing in report about These 4 x spikes]	Zinc	470/0	None, 4X

The samples were qualified JS#, where the # is the percent recovery of that particular analyte. A low matrix spike recovery indicates a possible slight low bias to the reported result and a high spike indicates a potential high bias to the data proportional to the spike recovery. When the spike is less than four times (4X) the concentration of the analyte in the parent sample, no qualification is required as the recovery is statistically invalid. The CLP limits are used for validation.

L47726 had 3 MS/MSDs with sample L47726-01 run twice. It was within limits for the first QC set and copper was at 71.3% and 109% for the second analysis in a separate QC set. As there are 2 acceptable MS/MSD pairs for client samples, no qualification has been applied.

L47715 had MS/MSDs with sample L47715-15 run twice. It was outside of QC limits in the first QC set at 73.3% and 74.7% and within QC limits for the second analysis at 94.4% and 93.3%. As there is an acceptable MS/MSD pair for the client samples, no qualification has been applied.

L58640 has Selenium outside of Laboratory QC limits at 117 and 118%; however, the recoveries are within the CLP limits.

L47828 and L54005 have Sulfate outside of Laboratory QC limits at 79% and 118%, respectively; however, the recoveries are within the CLP limits.

L56408 had multiple analytes outside of laboratory QC limits; however, the recoveries were within the CLP Limits except as noted in the above table.

C. The MS/MSD samples were client samples

Yes ☒ No ☐

There are often several preparation batches and therefore several MS/MSD pairs in many data sets. A client sample has been used for qualification when one is present. If a non-client sample has been used, it is noted in the table above.

VII. MATRIX DUPLICATE

A. Matrix duplicate was analyzed for every analysis performed and for every 20 samples or for every matrix whichever is more frequent.

Yes ☒ No ☐

Either a matrix duplicate or an MS/MSD was run.

B. The matrix duplicate relative percent difference (RPD) were within the limits defined in the contract or the CLP 20% for water and 35% for soil, or \pm RL for water results $< 5 \times$ RL ($\pm 2 \times$ RL for soils).

Yes ☐ No ☒

The following matrix duplicate RPD resulted in sample qualification.

SDG	QC set	Parent Sample	Analyte	RPD	Qualifier
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L45918 | 173689 | FIMST126-1-QA1(F) | Nickel | 174 | JD174 MS/MSD, JD143 (MD) |

Data are qualified JD#, where # is the value of the Relative Percent Difference (RPD) of the samples values. As the RPD increases, the matrix precision decreases

VIII. LABORATORY CONTROL SAMPLE

A. A Laboratory Control Sample (LCS) was analyzed for every analysis performed and for every 20 samples or for every matrix, whichever is more frequent.

Yes X No

B. The LCS percent recoveries were within the limits defined in the contract or the EPA limits of 80 – 120%.

Yes No X

The following LCS recoveries resulted in sample qualification.

SDG	QC set	Analyte	Recovery	Qualifier
L45832	173710	Zinc	107/125	JL125

The samples were qualified JL#, where # is the value of the percent recovery of the LCS from the true value. The data validation QC limit is 80% - 120% for inorganic waters. Data whose percent recovery is greater than 120% could possibly be biased high with respect to the extent of the recovery. Undetected data are not qualified for high LCS recoveries. Per the QAPP, the CLP limits are used for validation.

IX. SERIAL DILUTION.

A serial dilution of 1:4 was performed for 1/20 samples when an analyte is > 50 X IDL (> 100 X for ICPMS) [Many of the MWH reports say "NA" for serial dilution. This is a required QC sample, although it may not be applicable for low level results as noted in the comments]

Yes No X

Serial dilutions have not been reported for some of the data sets as noted below. Non-linear chemical or matrix effects cannot be determined. For most data sets, reported values are less than 50 x IDL and would not be impacted, but the QC sample is still required to be analyzed and reported.

Not reported:

L47720 (no detected data and the serial dilution would not apply)

L56513 total and dissolved analyses. (only calcium and magnesium are > 50 x IDL)

L47824 dissolved analysis.

L45774 dissolved analysis.

L54005 total and dissolved analyses.

L45773 total and dissolved analyses.

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B. And the % Difference between the diluted sample results is $\leq 10\%$ when the parent sample value is $> 50 \times \text{IDL}$ ($100 \times$ for ICPMS).

Yes ☐ No ☒ NA ☐

The following Serial Dilution %D resulted in sample qualification. [No values have been reported]

SDG	QC Set	Parent Sample	Analyte	%D	Qualifier
L47669	180285	VEMST067-0-C(5)	Molybdenum	35	None, 100X
L45832	173710	051404SEMST090-0	Nickel	44.5	JE44
	173957	051404SEMST027-0	Nickel	14.7	None, 100X
L45918	173689	050804FIMST126-2-0	Nickel	23.5	None, 100X
L47715	181460	SSMST068-0-C(5)	Cadmium	[28.9	None, 100X
	180983	SSMST068-0-C(5)	Chromium	26.9	JE27]
	180983	SSMST068-0-C(5)	Molybdenum	25.5	None, 100X
	181126	SSMST068-0-C(5)	Molybdenum	30.3	None, 100X
	181126	SSMST068-0-C(5)	Nickel	22	JE22
	180983	SSMST068-0-C(5)	Zinc	27.5	JE28
L47726	182382	SSMST229-0-C(5)	Copper	[20	JE20]
		SSMST236-0-C(9)	Nickel	51	JE51
		SSMST236-0-C(9)	Chromium	[14.6	JE14.6]

Data is qualified JE#, where # is the Percent Difference (%D) between the original sample and the diluted sample results. The %D limit is 90 – 110% only if the reported value of the metal is $>50 \times \text{IDL}$ ($100 \times$ for ICPMS). Values below this are not qualified. When the %D is above the QC limits, it is possible reported data are biased high due to non-linear chemical or matrix interference.

X. INSTRUMENT DETECTION LIMITS

A. The Instrument Detection Limits have met the Quarterly criteria.

Yes ☒ No ☐

Quarterly IDL reports are not required of Method 6010, but must be present for CLP. The actual levels that must be met are almost always pre-negotiated between the client and the lab before the analyses are performed.

And all sample results have met the required detection limits (CRDL).

Yes ☒ No ☐

XI. FIELD QC

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If Field duplicates or Performance Check Compounds were identified, they met the RPD guidance of 35% RPD for water or 50% RPD for soils. For values $<5 \times \text{RL}$, a difference of $\pm 2 \times \text{RL}$ is used for water and $\pm 4 \times \text{RL}$ is used for soils. Data are not qualified for field duplicates as the final decision on field precision is made by the project manager.

Yes ☐ No ☒ NA ☐

Field duplicates were not identified to the reviewers.

XIII. CALCULATIONS

A. Data algorithm for calculations were checked when required and data were correctly reported.

Yes ☒ No ☐ NA ☐

Per the raw data check.

B. Appropriate dilution factors were applied to the calculated sample concentrations.

Yes ☒ No ☐

OVERALL ASSESSMENT OF THE CASE

The data are considered fully useable for project purposes with consideration of the follow qualification or comments.

Deliverables

Water samples were analyzed for up to 12 ICP metals and 11 ICP/MS metals, plus mercury, selenium and sulfate parameters. Most water sets also contained total and dissolved analyses with associated distinct QC sets (days of analysis with separate QC and calibration). There were also a number of data sets that contained multiple runs (QC sets) for one of more of the requested analytes. The associated QC batch of these multiple QC sets was used in qualification of data. The following is a breakdown of matrices submitted.

Method	Water	Water	Soil	Plant	Animal	Veg
ICP &/or ICPMS Metals	Total 80	Diss. 49	32	9	4	2
Se by AA	108	59	42	33	18	2
SO4	33					

The standard deliverable for analytical data is to provide summary tables for each of the following QC items: calibrations, low level standard check, blanks, Matrix spikes and matrix duplicates (or MS dups), post digestion spikes, LCS, serial dilution, ICP ICS and ICPMS Internal Standards as well as tables for the current MDLs and RLs. The laboratory has instead generated data lists for each analyte including the above items when they were actually analyzed. As many of the above items are missing from the data sets, and are not consistently missing for all the analytes in the data set, the complexity of the review was significant and time consuming. A

listing of missing QC is contained in the specific QC sections of the report.

Holding Time

Samples were received within 1 – 3 days of collection, but not analyzed within contractual holding time for L47824.

The following validation holding times had been exceeded.

SDG	QC Set	Sample	Analyte	Date Sampled	Date Analyzed	Qualifier
L47824	180026	SWMST275-0-F	Sulfate	9/14/04	10/19/04	JH5
L54005	199814	103005GWMMW004-2-F	Sulfate	10/30/05	11/28/05	JH1
		103005GWMMW004-3-F	Sulfate	10/30/05	11/28/05	JH1

Data is qualified JH#, where # is the number of days exceeding the holding time. Data could possibly be biased low as the number of days exceeds the allowed holding time.

Chain of Custody and Sample Integrity

For L47720, the temperature was 15.8° C. These samples are noted as 'veg', but treated for preparation and reporting as aqueous. They are also reported at pH < 2 as if they are water. If these are not water-type matrices, they should be kept at < 4° C. There is a note that the project manager is to be contacted, but there is no follow up communication. As these appear to be of some type of water matrix, no qualification is added. One of the samples is an equipment blank, which would be a water.

L47720: There are 10 samples listed on the chain, but only 2 are reported. There is nothing in the narrative or any noted communication to explain why all samples are not reported. There is no method of analysis listed on the chain. In the box which usually has the requested method of analysis, it only lists "Veg".

L56513: There are 2 samples on the chain that are noted as not being received and it is noted that the client was not notified.

For the majority of the data sets there is no method of analysis listed on the chain. As almost all chains are impacted, they have not been listed here. In the box which usually has the requested method of analysis, it only lists items like "soil, SW total, SW dissolved, fish, etc". The reviewer cannot verify that that required or requested analyses have been performed.

Chains contain items that have been blocked out rather than one-line cross out and no initials are present. The chains have a gap from date of relinquishment to date of laboratory receipt. Some of the chains note a FedEx courier and some do not, none have a FedEx airbill number for tracking of the sample custody. The chains need to be updated and completed for the project record.

Calibration and Tunes

The following analytes exceed the QC limits for the initial calibration:

SDG	QC Set	Analyte	Recovery (%)	Qualifier
L47824	179843	Cadmium	110.3	JC110
L45918	175879	Zinc	110.5	JC110
L47715	181460	Chromium	110.4	JC110

Data is qualified JC#, where # is the percent recovery of the Initial Calibration Verification (ICV) standard from the true value. The limit is 90% - 110%. Data whose percent recovery is less than 90% could possibly be biased low with respect to the extent of the recovery. Data whose percent recovery is greater than 110% could possibly be biased high with respect to the extent of the recovery. Undetected data are not qualified for high ICV recoveries. These are minimal exceedences and the data are not expected to be impacted.

Per the full raw data review of 2 of the data packages:

L47726: Only the tune from 11/24/04 is reported. There are no tunes for 11/18, 11/29 or 12/05 reported analyses. Full evaluation of calibration and instrument tuning cannot be determined.

L56513: Full tunes are reported for 12/ 19 and 22/06.

There is no evidence in the raw data that the oxides are analyzed or are used as required to minimize interferences.

There is no evidence in the raw data that the interfering oxide and chloride molecules are analyzed for or are used as required to minimize interferences. All calibrations, LCS were will within limits which could indicate that the computerized correction for chlorides and oxides has been performed.

CRDL

CRDLs are not consistently reported. This is called a PQV by the laboratory. There can be a PQV for one analyte in a data set, but not for others.

L56513: CRI not reported for most of the ICPMS analytes including: Cd, Cr, Pb, Mn, Ni; for ICP there is no CRI for dissolved Mn; no CRI for selenium or mercury.

L46912, L47351, L46807, L46940, L58644, and L58640: no CRI for Se.

L47726: no CRI for any analytes.

L47669: no CRI for any analytes.

L47824: no CRI for Cd, Cr, Ni, Se, V and Zn.

L45774: no CRI for Cd, Cr, Mg, Ni, Se, V, and Zn.

L54005: no CRI for Cd, Cr, Mn, Ni, Se, V, and Zn.

L45832: no CRI for Cd, Cr, Ni, Se, V, and Zn.

L45918: no CRI for Cd, Ni, Se, V, and Zn.

L47715: no CRI for Cd, Cr, Cu, Mo, Ni, Se, V, and Zn.

L45773: no CRI for Cd, Cr, Ni, Se, V, and Zn.

L47720: Per the full raw data review, no CRI (PQV) was reported, but there is a PQV in the raw data. The PQV has no final results reported, but the CPS values have been compared to the lowest reported standard (Std 3) and potential values extrapolated. The ability of the instrumentation to reach the low level standard is not acceptable for cadmium and molybdenum. The raw data were reviewed for the 2 client samples. Instrument counts in the range of the PQV were not reported and the undetected values appear to be verified although the MDL may not be valid. Undetected values at the reporting limit should be assumed for these samples.

The low CRDL standard is required to ensure accuracy of low-level response. There is no qualification required for lack of the CRI, but results reported >MDL but below the RL could be estimated values.

Blanks

Below is a table of analytes that were found in the calibration blanks.

SDG	QC batch	Analyte	Result	Qualifier
L56513	206448	Arsenic (dis)	0.00073	UCB.00073
		Lead (dis)	0.00014	None
	206701	Thallium	0.00015	None, ND
L54005	199080	Cadmium	0.00012	None, ND
L56408	205973	Arsenic (tot)	0.00067	None, ND

Data have been qualified UCB#, where # is the value of the associated blank. Data are qualified only when sample results are <5 X blank. When data are >5 X the blank and require no qualification, it is indicated as such in the table. Data are fully usable as undetected values.

Below is a table of analytes that were found in the preparation blanks. Note that preparation blanks are not required for dissolved metals. The following data sets did not have an identified preparation blank. Contamination cannot be verified and false detected values could be reported.

L56513, L54005, L45773, L47720 – An LRB is reported. Full review of the raw data preparation tables for one data set has confirmed this is a preparation blank that is carried through the entire preparation process.

SDG	QC Set	Analyte	Result	Qualifier
L47726	180947	Chromium	2.77	None
	180947	Molybdenum	0.094	UB.094
	180947	Vanadium	3.91	None
	181486	Chromium	3.47	None
	182088	Chromium	0.083	None

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SDG	QC Set	Analyte	Result	Qualifier
	181486	Copper	1.98	None
	182021	Copper	2.57	None
	182382	Copper	2.19	UB2.19
L47824	179842	Cadmium	0.00011	None, ND
		Chromium	0.00021	None, ND
		Nickel	0.00024	None, 5X
L54005	198985	Chromium	0.00021	UB.00021
L45832	173710	Chromium	0.072	None, 5X
		Nickel	0.89	None, 5X
		Vanadium	0.219	None, 5X
	173957	Chromium	0.051	None, 5X
		Vanadium	0.323	None, 5X
L45918	173797	Vanadium	0.076	UB.076
	175879	Vanadium	0.248	UB.248
L47715	181460	Chromium	0.727	None, 5X
	180983	Molybdenum	0.275	None, 5X
	181126	Molybdenum	0.052	None, 5X
	181460	Vanadium	1.242	None, 5X

Analytes reported as contaminants in the preparation blank are qualified UB# in the affected samples, where # is the value of the blank corrected to the units of the sample. Sample detects whose values are less than 5x blank are qualified and are fully usable as undetected values at that level. 'None' indicates that undetected values or values > 5 x blank were reported. Data are fully usable as undetected values.

Below is a table of analytes that were found in the field blanks.

SDG	Blank	Analyte	Result	Qualifier
L56513	050906SWMST088-EQ-F	Chromium	0.0002	None
		Manganese	0.0015	None
		Zinc	0.005	None
L45774	051204SWMSP011-EQ-F	Sodium	0.6	UFB.6
		Zinc	0.002	UFB.002
L45773	051204SEMSP021-EQ-U	Calcium	0.4	None
	051204SEMSP021-EQ-U	Chromium	0.0002	UFB.0002
	051204SEMSP011-EQ-U	Sodium	0.5	UFB.5
	051204SEMSP021-EQ-U	Vanadium	0.000009	None

Data have been qualified UFB#, where # is the value of the associated blank. Data are qualified only when sample results are <5 X blank. When data are >5 X the blank and require no qualification, it is indicated as such in the table. Data are fully usable as undetected values.

Matrix Spike/Matrix Spike Duplicates

The following matrix spike recoveries resulted in sample qualification.

SDG	Matrix	QC set	Parent Sample	Analyte	Result	Qualifier
L58644	Water	213089	050406SWMSP059-0-U	Selenium	74/85	JS74
			050406SWMSP010-0-U	Selenium	85/240	None, 4X
L47669	Plant	180285	VEMST069-0-C(5)	Zinc	54/56	JS54
L46940	Water	177338	Non-Client Sample	Selenium	70/67	JS67
L46807	Plant	176602	VEMWD082-1-C(6)	Selenium	86/61	None, 4X
			Non-Client Sample	Selenium	55/100	None, 4X
L45832	Soil	173710	Non-Client Sample	Cadmium	44/50	JS44
			Non-Client Sample	Chromium	0/0	None, 4X
			Non-Client Sample	Nickel	52/91	None, 4X
			Non-Client Sample	Vanadium	0/0	None, 4X
			Non-Client Sample	Zinc	0/0	None, 4X
		173957	Non-Client Sample	Chromium	0/0	None, 4X
			Non-Client Sample	Nickel	61/100	None, 4X
			Non-Client Sample	Vanadium	0/0	None, 4X
L45918	Fish	173689	FIMST126-1-QA1(F)	Nickel	1200/35	JS1200
			050804FIMST126-1-QA2	Zinc	35/0	None, 4X
			050804FIMST126-1-QA3	Zinc	39/314	None, 4X
			050804FIMST126-2-0	Zinc	61/0	None, 4X
L47715	Soil	181460	SSMSG005-1-C(5)QA1	Chromium	133/149	None, 4X
			SSMSG005-1-C(5)QA1	Vanadium	131/141	None, 4X
		180983	SSMSG005-1-C(5)QA1	Zinc	238/191	None, 4X
L47726	Soil					Run 2x, ok 2 nd , no Q
		182382	SSMST236-0-C (9)	Copper	71/109	
		182088	SSMST236-0-C (9)	Chromium	137/ 193	None, 4x
		180947	SSMST022-1-C (6)	Chromium	127/ 138	None, 4x
		181486	SSMST022-1-C (6)	Vanadium	135/ 127	None, 4x
L56408	Water	205973	Non-Client Sample	Arsenic	141/122	None, ND
			Non-Client Sample	Nickel	0/0	None, 4X
			Non-Client Sample	Uranium	234/0	None, 4X
			Non-Client Sample	Vanadium	97/0	None, 4X

		Non-Client Sample	Zinc	470/0	None, 4X
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The samples were qualified JS#, where the # is the percent recovery of that particular analyte. A low matrix spike recovery indicates a possible slight low bias to the reported result and a high spike indicates a potential high bias to the data proportional to the spike recovery. When the spike is less than four times (4X) the concentration of the analyte in the parent sample, no qualification is required as the recovery is statistically invalid. The CLP limits are used for validation.

L47726 had 3 MS/MSDs with sample L47726-01 run twice. It was within limits for the first QC set and copper was at 71.3% and 109% for the second analysis in a separate QC set. As there are 2 acceptable MS/MSD pairs for client samples, no qualification has been applied.

L47715 had MS/MSDs with sample L47715-15 run twice. It was outside of QC limits in the first QC set at 73.3% and 74.7% and within QC limits for the second analysis at 94.4% and 93.3%. As there is an acceptable MS/MSD pair for the client samples, no qualification has been applied.

L58640 has Selenium outside of Laboratory QC limits at 117 and 118%; however, the recoveries are within the CLP limits.

L47828 and L54005 have Sulfate outside of Laboratory QC limits at 79% and 118%, respectively; however, the recoveries are within the CLP limits.

L56408 had multiple analytes outside of laboratory QC limits; however, the recoveries were within the CLP Limits except as noted in the above table.

The following matrix duplicate RPD resulted in sample qualification.
ing matrix duplicate RPD resulted in sample qualification.

SDG	QC set	Parent Sample	Analyte	RPD	Qualifier
L45918	173689	FIMST126-1-QA1(F)	Nickel	174	JD174 MS/MSD, JD143 (MD)

Data is qualified JD#, where # is the value of the Relative Percent Difference (RPD) of the samples values. As the RPD increases, the matrix precision decreases.

LCS

The following LCS recoveries resulted in sample qualification.

SDG	QC set	Analyte	Recovery	Qualifier
L45832	173710	Zinc	107/125	JL125

The samples were qualified JL#, where # is the value of the percent recovery of the LCS from the true value. The data validation QC limit is 80% - 120% for inorganic waters. Data whose percent recovery is greater than 120% could possibly be biased high with respect to the extent of

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the recovery. Undetected data are not qualified for high LCS recoveries. Per the QAPP, the CLP limits are used for validation.

Serial Dilution

Serial dilutions have not been reported for some of the data sets as noted below. Non-linear chemical or matrix effects cannot be determined. For most data sets, reported values are less than 50 x IDL and would not be impacted, but the QC sample is still required to be analyzed and reported.

Not reported:

L47720 (no detected data and the serial dilution would not apply)

L56513 total and dissolved analyses. (only calcium and magnesium are > 50 x IDL)

L47824 dissolved analysis.

L45774 dissolved analysis.

L54005 total and dissolved analyses.

L45773 total and dissolved analyses.

The following Serial Dilution %D resulted in sample qualification.

SDG	QC Set	Parent Sample	Analyte	%D	Qualifier
L47669	180285	VEMST067-0-C(5)	Molybdenum	35	None, 100X
L45832	173710	051404SEMST090-0	Nickel	44.5	JE44
	173957	051404SEMST027-0	Nickel	14.7	None, 100X
L45918	173689	050804FIMST126-2-0	Nickel	23.5	None, 100X
L47715	181460	SSMST068-0-C(5)	Cadmium	28.9	None, 100X
	180983	SSMST068-0-C(5)	Chromium	26.9	JE27
	180983	SSMST068-0-C(5)	Molybdenum	25.5	None, 100X
	181126	SSMST068-0-C(5)	Molybdenum	30.3	None, 100X
	181126	SSMST068-0-C(5)	Nickel	22	JE22
L47726	180983	SSMST068-0-C(5)	Zinc	27.5	JE28
	182382	SSMST229-0-C(5)	Copper	20	JE20
		SSMST236-0-C(9)	Nickel	51	JE51
		SSMST236-0-C(9)	Chromium	14.6	JE14.6

Data is qualified JE#, where # is the Percent Difference (%D) between the original sample and the diluted sample results. The %D limit is 90 – 110% only if the reported value of the metal is >50 X IDL (100X for ICPMS). Values below this are not qualified. When the %D is above the QC limits, it is possible reported data are biased high due matrix interference due to non-linear matrix or chemical interferences.

Interference Check Samples (ICS)

The ICS QC requirement has not been met for some of the data sets as noted below. When the ICS is not reported, it cannot be verified that the interference from high-level analytes has been

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adequately compensated for in the computer software. Only samples that have high levels of the major cations (Al, Fe, Ca, Na, K) would be most impacted. For the analyses with limited list of analytes, the potential interfering analytes are not in the project list and even if the ICS were out of limits, the potential impact could not be evaluated unless the raw data were re-evaluated for the interfering analytes.

L56513: full list of analytes requested, no ICS reported.

L47824: no ICS reported.

L45774: no ICS reported.

L54005: no ICS reported

L45773: no ICS reported.

L47720: no ICS reported